



# **VERIFIED ENGLISH TRANSLATION OF PRIORITY DOCUMENT JP 2001-262702**



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DECLARATION OF ACCURACY OF TRANSLATION  
IN LIEU OF SWORN TRANSLATION (37 C.F.R. 1.55 & 1.68)

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(1) I am fully conversant both with the Japanese and English languages.

(2) I have carefully compared the attached English language translation of Japanese Patent Application Number 2001-262702, filed August 31, 2001, with the original Japanese-language patent application.

(3) The translation is, to the best of my knowledge, and belief, an accurate translation from the original into the English language.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the matter with which this translation is used.

Date: October 13, 2006

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Applicant(s) :	Mitsubishi Paper Mills, Ltd.

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[Title of the invention] Ink-jet recording material and process for preparing the same

[Scope of claim for patent]

[Claim 1] An ink-jet recording material wherein at least one ink-receptive layer is applied on a support in which the both surfaces of an base paper are coated with polyolefin resin, wherein the ink-receptive layer comprises inorganic fine particles having an average primary particle size of 30 nm or less and a hydrophilic binder, and the ink-jet recording material is so cut that a paper feeding direction of a printer is at right angle to a flowing direction at a time of coating the ink-receptive layer.

[Claim 2] The ink-jet recording material according to Claim 1, wherein the inorganic fine particles are at least one of fumed silica and alumina hydrate.

[Claim 3] The ink-jet recording material according to Claim 1 or 2, wherein a mass ratio of the hydrophilic binder to the inorganic fine particles is 0.40 or less.

[Claim 4] The ink-jet recording material according to any one of Claims 1 to 3, wherein the ink-receptive layer contains a hardener for the hydrophilic binder.

[Claim 5] A process for preparing an ink-jet recording material wherein an ink-receptive layer comprising inorganic fine particles having an average primary particle size of 30 nm or less and a hydrophilic binder is applied on a support in which the both surfaces of an base paper are coated with polyolefin resin, which comprises coating the ink-receptive layer using the support rolled with the surfaces to be coated with the ink-receptive layer outside, and then, rolling the recording material with the ink-receptive layer side outside, and cutting the recording material so that a paper feeding direction of a printer is right angle to a flowing direction at a time of coating the ink-receptive layer.

[Detailed description of the invention]

[0001]

[Technical field to which the invention belongs]

The present invention relates to an ink-jet recording material, particularly to an ink-jet recording material having good texture and glossiness, and causing no head rubbing at the time of printing by a printer.

[0002]

[Prior art]

As a recording material to be used for an ink-jet recording system, there are known a recording material in which an ink-receptive layer comprising a hydrophilic polymer or a porous ink-receptive layer comprising a pigment such as amorphous silica and a water-soluble binder is provided on a normal paper or a support referred to as ink-jet recording paper.

[0003]

It has been proposed a recording material in which a hydrophilic polymer such as starch, polyvinyl alcohol, etc. is provided on a support as disclosed in, for example, Kokai (unexamined patent publication) No. Sho. 56-080489, No. Sho. 59-174381, No. Sho. 60-220750, No. Sho. 61-32788, No. Sho. 63-160875, No. Hei. 3-69388 and the like.

[0004]

It has been proposed a recording material in which a silicon-containing pigment such as silica is applied on a paper support with a water-based binder, as disclosed in, for example, Kokai (unexamined patent publication) No. Sho. 55-51583, No. Sho. 56-157, No. Sho. 57-107879, No. Sho. 57-107880, No. Sho. 59-230787, No. Sho. 62-160277, No. Sho. 62-184879, No. Sho. 62-183382, No. Sho. 64-11877 and the like.

[0005]

Also, in Kokai (unexamined patent publication) No. Hei. 3-56552, No. Hei. 2-188287, No. Hei. 10-81064, No. Hei. 10-119423, No. Hei. 10-175365, No. Hei. 10-193776, No. Hei. 10-203006, No. Hei. 10-217601, No. Hei. 11-20300, No. Hei. 11-20306, No. Hei. 11-34481 and the like, there have been disclosed ink-jet recording materials obtained by using

synthetic silica fine particles prepared by a gas phase process (hereinafter referred to as "fumed silica"). Moreover, in Kokai (unexamined patent publication) No. Hei. 2-276671, No. Hei. 3-67684, No. Hei. 3-251488, No. Hei. 4-67986, No. Hei. 4-263983, No. Hei. 5-16517 and the like, there have been disclosed ink-jet recording materials obtained by using alumina hydrates. These fumed silica and alumina hydrates are ultrafine particles having a primary particle-average particle size of several nm to several tens nm, so that they have characteristics of giving good glossiness and ink-absorbability. In recent years, a photo-like recording material has earnestly been desired, and the texture, feeling and glossiness close to photography becomes more important. As such a recording material, there has been proposed a recording material in which an ink-receptive layer mainly consisting of the above-mentioned fine particles is applied on a water resistant support such as a polyolefin resin-coated paper same as a photograph (the both surfaces of base paper are coated with a polyolefin resin such as polyethylene), etc.

[0006]

In the ink-jet printer corresponding to a photo printer, a low-density ink has generally been used alone or in combination with a high-density ink to form a photo-like image. To obtain an image by using such a low-density ink, it is necessary to discharge a large amount of the ink, so that a recording material is required to have very high ink-absorbability. A polyolefin resin-coated paper is a water-resistant support and ink-receptive layer alone has necessary to absorb ink, so that a large amount of ink-receptive layer to be applied is inevitably required. However, in an ink-jet recording material in which a large amount of an ink-receptive layer is applied, curl to the direction of a printed surface side (hereinafter referred to as "plus curl") due to shrinkage of the ink-receptive layer by drying tends to be remarkable, so that a phenomenon that the recording material and an ink-jet head are contacted to each other at the time of

printing(hereinafter referred to as "head rubbing") frequently occurs.

[0007]

On the other hand, accompanying with speeding up and high-quality picture technologies of ink-jet printer, clearance of the ink-jet head and the recording sheet tends to be little in order to improve impact precision of ink-jet ink to a recording material. Also, in recent years, a printer which can carry out four edges-less printing with a sheet-feed material has been sold. In such a printer, the problem of head rubbing is more likely to arise. Particularly in a polyolefine resin coated paper which is photo-like and has high rigidity, when head rubbing is caused, it not only blows up a printed image but also leads to damage of the ink-jet head, so it is a difficult problem.

[0008]

[Problems to be solved by the invention]

Accordingly, an object of the present invention relates to an ink-jet recording material, and particularly, is to provide an ink-jet recording material having a good texture and glossiness and causing no head rubbing at the time of printing.

[0009]

[Means to solve the problem]

The present inventors have earnestly studied, and as a result, they have found that, in an ink-jet recording material wherein an ink-receptive layer comprising inorganic fine particles and a hydrophilic binder is provided on a support in which the both surfaces of an base paper are coated with polyolefin resin, manner of plus curl due to environmental change in a paper feeding direction of a printer varies depending on a cutting direction at the time of cutting, and the manner of plus curl materially affects head rubbing at the time of printing with a printer. Conclusively, the present inventors have found that the above objects can be accomplished by following means.



[0010]

(1) An ink-jet recording material wherein at least one ink-receptive layer is applied on a support in which the both surfaces of an base paper are coated with polyolefin resin, wherein the ink-receptive layer comprises inorganic fine particles having an average primary particle size of 30 nm or less and a hydrophilic binder, and the ink-jet recording material is so cut that a paper feeding direction of a printer is at right angle to a flowing direction at a time of coating the ink-receptive layer.

(2) The ink-jet recording material according to above 1, wherein the inorganic fine particles are at least one of fumed silica and alumina hydrate.

(3) The ink-jet recording material according to above 1 or 2, wherein a mass ratio of the hydrophilic binder to the inorganic fine particles is 0.40 or less.

(4) The ink-jet recording material according to any one of above 1 to 3, wherein the ink-receptive layer contains a hardener of the hydrophilic binder.

(5) A process for preparing an ink-jet recording material wherein an ink-receptive layer which comprises inorganic fine particles having an average primary particle size of 30 nm or less and a hydrophilic binder is applied on a support in which the both surfaces of an base paper are coated with polyolefin resin, which comprises coating the ink-receptive layer using the support rolled with the surfaces to be coated with the ink-receptive layer outside, and then, rolling the recording material with the ink-receptive layer side outside, and cutting the recording material so that a paper feeding direction of a printer is right angle to a flowing direction at a time of coating the ink-receptive layer.

[0011]

For example, in Japanese provisional Patent Publication No. 2000-263926 as a known document in which a cutting direction at the time of cutting is defined, there is proposed

a ink-jet recording paper wherein an undercoating layer is optionally applied on a paper support and a gloss layer is further applied, thickness of the paper is 100 to 300  $\mu\text{m}$  and a rigidity (J. TAPPI No. 40) in a paper feeding direction of a printer is 200 to 1000 mgf, and the ink-jet recording paper is so cut that a paper feeding direction of a printer is at right angle to a flowing direction at a time of papermaking of the paper support. The ink-jet recording paper has relatively-high glossiness and good transportability, however, the paper support absorbs a ink and wave wrinkle likely to be caused, so it has problems that it has poor texture as an alternative to a photograph and likely to cause head robbing due to the wave wrinkle. Accordingly, the ink-jet material is absolutely different from the purport of the present invention.

[0012]

[Embodiment of the invention]

In the following, the present invention will be explained in detail.

In an ink-jet recording material of the present invention, no ink is absorbed by the support whereby no wrinkle causes and a good photo-like texture and glossiness can be obtained. When such a support is to be used, it is necessary to absorb all the discharged ink by the ink-receptive layer, so that a large amount of the ink-receptive layer to be coated and a high void ratio are required. When such a coating layer having a large amount to be coated and high void ratio is applied, plus curl having a curvature of right angle to a flowing direction at a time of coating the ink-receptive layer generally occurs due to a shrink of the coated layer by drying. Further, after coating and drying, plus curl also occurs in the similar direction depending on an environmental change such as temperature and humidity changes, particularly in low temperature and low humid environment. When such an recording paper is so cut that a paper feeding direction of a printer (in most of commercially available ink-jet printers, it is recommended to feed a paper in a

longitudinal direction of the paper) is at right angle to a flowing direction at a time of coating the ink-receptive layer, plus curl having a curvature of right angle to paper feeding direction of printer, or scanning direction of printing head occurs, so that paper edges dose not extremely lift up and no head rubbing causes at a time that print is carried out on a paper which is retained just anterior to a printing head (at a time of printing on anterior edge of paper) and print is carried out on a paper which is retained just posterior to a printing head (at a time of printing on posterior edge of paper). When an ink-jet recording paper is so cut that a paper feeding direction of a printer becomes flowing direction at a time of coating the ink-receptive layer, plus curl which is right angle to paper feeding direction of printer, that is, has a curvature in a scanning direction of printing head occurs, so that paper edges extremely lifts up and head rubbing likely to cause at a time of printing on anterior edge of paper and at a time of printing on posterior edge of paper, which is not favorable.

[0013]

As the inorganic fine particles in the present invention, known inorganic fine particles having an average primary particle size of 30 nm or less are preferred in order to heighten glossiness. Furthermore, it is particularly preferred to use at least one of fumed silica and alumina hydrate as the inorganic fine particles in order to heighten ink absorbability and glossiness.

[0014]

Fumed silica to be preferably used in the present invention is also called to as the drying method silica, and it can be generally prepared by a flame hydrolysis method. Specifically, it has been generally known a method in which silicon tetrachloride is burned with hydrogen and oxygen. In place of silicon tetrachloride, silanes such as methyl trichlorosilane and trichlorosilane can be used alone or in combination with silicon tetrachloride. The fumed silica is

commercially available from Nippon Aerosil K.K. (Japan) under the trade name of Aerosil, and K.K. Tokuyama (Japan) under the trade name of QS type, etc. The fumed silica is generally present in the form of secondary particles having a suitable void by aggregation. Thus, it is preferably used by pulverizing or dispersing with ultrasonic wave, a high-pressure homogenizer or a counter collision type jet pulverizer until an average particle size of the secondary particles becomes 50 to 300 nm or so since it gives good ink-absorbability and glossiness.

[0015]

The alumina hydrate in the present invention is represented by the structural formula of  $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  ( $n=1$  to  $3$ ). When  $n$  is 1, it represents alumina hydrate having a boehmite structure, and when  $n$  is larger than 1 and less than 3, it represents alumina hydrate having a pseudo boehmite structure. It can be prepared by the conventionally known preparation method such as hydrolysis of aluminum alkoxide such as aluminum isopropoxide, etc., neutralization of an aluminum salt with an alkali, hydrolysis of an aluminate, and the like. Alumina hydrates as described in, for example, Kokai (unexamined patent publication) No. Hei. 2-276671, No. Hei. 3-67684, No. Hei. 3-251488, No. Hei. 4-67986, No. Hei. 4-263983, No. Hei. 5-16517 and the like may be optionally used.

[0016]

The average primary particle size of the inorganic fine particles in the present invention can be obtained from an observation of dispersed particles by an electron microscope, wherein for each of 100 particles existing in a predetermined area, a diameter of a circle whose area is equivalent to a projected area of each particle is taken as a particle diameter for that particle. The average primary particle size of the inorganic fine particles to be used in the present invention is preferably 30 nm or less, more preferably 5 to 30 nm since it gives good glossiness.

[0017]

In the ink-receptive layer, the inorganic fine particles are preferably contained in an amount of 8 g/m<sup>2</sup> or more, more preferably in the range of 10 to 30 g/m<sup>2</sup>. If the amount is less than such ranges, poor ink absorbability is obtained. A mass ratio of the hydrophilic binder to the inorganic fine particles is preferably 0.4 or less since good ink-absorbability can be obtained and plus curl due to shrinkage of the ink-receptive by drying layer and environmental changes can be made small.

[0018]

In the present invention, it is preferable to contain the inorganic fine particles in a principle ratio, that is, in an amount of 50% by mass or more, preferably 60% by mass or more, more preferably 65% by mass or more based on the total solid component of the ink-receptive layer.

[0019]

In the present invention, as the hydrophilic binder to be used in combination with the inorganic fine particles, various kinds of binders which are conventionally known can be used, and a hydrophilic binder which has high transparency and gives high permeability of ink is preferably used. For using the hydrophilic binder, it is important that the hydrophilic binder does not clog the voids by swelling at the initial stage of permeation of ink. From this point of view, a hydrophilic binder having a relatively low swellability at around the room temperature is preferably used. A particularly preferred hydrophilic binder is a completely or partially saponified polyvinyl alcohol or a cationic-modified polyvinyl alcohol.

[0020]

Among the polyvinyl alcohols, particularly preferred is partially or completely saponified polyvinyl alcohol having a saponification degree of 80% or more. A polyvinyl alcohol having an average polymerization degree of 200 to 5000 is preferred.

[0021]

Also, as the cationic-modified polyvinyl alcohol, there may be mentioned, for example, a polyvinyl alcohol having a primary to tertiary amino groups or a quaternary ammonium group in the main chain or side chain of the polyvinyl alcohol as described in Kokai (unexamined patent publication) No. Sho. 61-10483.

[0022]

The present invention is particularly preferable since, plus curl due to environmental changes becomes small and head rubbing is difficultly caused by using the above-mentioned hydrophilic binder in combination with a hardener. Specific examples of the hardener may include an aldehyde type compound such as formaldehyde and glutaraldehyde; a ketone compound such as diacetyl and chloropentanedione; bis(2-chloroethylurea)-2-hydroxy-4,6-dichloro-1,3,5-triazine; a compound having a reactive halogen as described in U.S. Patent No. 3,288,775; divinylsulfone; a compound having a reactive olefin as described in U.S. Patent No. 3,635,718; a N-methylol compound as described in U.S. Patent No. 2,732,316; an isocyanate as described in U.S. Patent No. 3,103,437; an aziridine compound as described in U.S. Patents No. 3,017,280 and No. 2,983,611; a carbodiimide type compound as described in U.S. Patent No. 3,100,704; an epoxy compound as described in U.S. Patent No. 3,091,537; a halogen carboxyaldehyde such as mucochloric acid, a dioxane derivative such as dihydroxydioxane, an inorganic crosslinking agent such as chromium alum, zirconium sulfate, boric acid and a borate, and they may be used independently or in combination of two or more. Of these, boric acid and a borate are particularly preferred.

[0023]

The ink-receptive layer according to the present invention preferably contain a cationic compound for the purpose of improving water resistance. As the cationic compound, there may be mentioned a cationic polymer and a water-soluble metallic compound.

[0024]

As the cationic compound to be used in the present invention, there may be mentioned, for example, a cationic polymer and a water-soluble metallic compound. As the cationic polymer, there may be preferably mentioned polyethyleneimine, polydiallylamine, polyallylamine, polyalkylamine, as well as polymers having a primary to tertiary amino group or a quaternary ammonium group as described in Kokai (unexamined patent publication) No. Sho. 59-20696, No. Sho. 59-33176, No. Sho. 59-33177, No. Sho. 59-155088, No. Sho. 60-11389, No. Sho. 60-49990, No. Sho. 60-83882, No. Sho. 60-109894, No. Sho. 62-198493, No. Sho. 63-49478, No. Sho. 63-115780, No. Sho. 63-280681, and Kokai (unexamined patent publication) No. Hei. 1-40371, No. Hei. 6-234268, No. Hei. 7-125411, No. Hei. 10-193776, etc. A molecular weight of these cationic polymers is preferably about 5,000 to 100,000.

[0025]

An amount of these cationic polymers to be used is 1 to 10% by mass, preferably 2 to 7% by mass based on the amount of the inorganic fine particles.

[0026]

The water-soluble metallic compound to be used in the present invention may include, for example, a water-soluble polyvalent metallic salt. As such a salt, there may be mentioned a water-soluble salt of a metal selected from the group consisting of calcium, barium, manganese, copper, cobalt, nickel, aluminum, iron, zinc, zirconium, chromium, magnesium, tungsten, and molybdenum. Specifically, such a water-soluble metallic compound may include, for example, calcium acetate, calcium chloride, calcium formate, calcium sulfate, barium acetate, barium sulfate, barium phosphate, manganese chloride, manganese acetate, manganese formate dihydrate, ammonium manganese sulfate hexahydrate, cupric chloride, copper (II) ammonium chloride dihydrate, copper sulfate, cobalt chloride, cobalt thiocyanate, cobalt sulfate, nickel sulfate hexahydrate, nickel chloride hexahydrate,

nickel acetate tetrahydrate, ammonium nickel sulfate hexahydrate, amide nickel sulfate tetrahydrate, aluminum sulfate, aluminum sulfite, aluminum thiosulfate, poly(aluminum chloride), aluminum nitrate nonahydrate, aluminum chloride hexahydrate, ferrous bromide, ferrous chloride, ferric chloride, ferrous sulfate, ferric sulfate, zinc bromide, zinc chloride, zinc nitrate hexahydrate, zinc sulfate, zinc phenolsulfonate, zirconium acetate, zirconium chloride, zirconium oxychloride octahydrate, zirconium hydroxychloride, chromium acetate, chromium sulfate, magnesium sulfate, magnesium chloride hexahydrate, magnesium citrate nonahydrate, sodium phosphotungstate, tungsten sodium citrate, 12-tungstophosphoric acid n-hydrate, 12-tungstosilicic acid 26-hydrate, molybdenum chloride, 12-molybdophosphoric acid n-hydrate, etc.

[0027]

Also, as the cationic compound, there may be mentioned a basic poly(aluminum hydroxide) compound which is an inorganic aluminum-containing cationic polymer. The basic poly(aluminum hydroxide) compound is a water-soluble poly(aluminum hydroxide), a main component of which is represented by the following formula (A), (B) or (C), and which contains a polynuclear condensed ion which is basic and a polymer in a stable form, such as  $[\text{Al}_6(\text{OH})_{15}]^{3+}$ ,  $[\text{Al}_8(\text{OH})_{20}]^{4+}$ ,  $[\text{Al}_{13}(\text{OH})_{34}]^{5+}$ ,  $[\text{Al}_{21}(\text{OH})_{60}]^{3+}$ , etc.

[0028]

$[\text{Al}_2(\text{OH})_n\text{Cl}_{6-n}]_m$  Formula (A)

$[\text{Al}(\text{OH})_3]_n\text{AlCl}_3$  Formula (B)

$\text{Al}_n(\text{OH})_m\text{Cl}_{(3n-m)}$   $0 < m < 3n$  Formula (C)

[0029]

These compounds are commercially available from Taki Chemical, K.K., Japan under the trade name of poly(aluminum chloride) (PAC, trade name) as a water treatment agent, from Asada Chemical K.K., Japan under the trade name of poly(aluminum hydroxide) (Paho, trade name), from K.K. Riken Green, Japan under the trade name of Pyurakemu WT (trade name)



and from other manufacturers with the same objects whereby various kinds of grades can be easily obtained. In the present invention, these commercially available products may be used as such. Of these products, there is a product having an unsuitably low pH. In such a case, it may be used by optionally adjusting the pH of the product.

[0030]

In the present invention, an amount of the above-mentioned water-soluble metallic compound in the ink-receptive layer is  $0.1 \text{ g/cm}^2$  to  $10.0 \text{ g/cm}^2$ , preferably  $0.2 \text{ g/cm}^2$  to  $5.0 \text{ g/cm}^2$ .

[0031]

The above-mentioned cationic compound may be used in combination of two or more kinds. For example, there may be used the cationic polymer and the water-soluble metallic compound in combination.

[0032]

Respective layers of the ink-receptive layer in the present invention may preferably contain various kinds of oil droplets to improve brittleness of a film. As such oil droplets, there may be mentioned a hydrophobic organic solvent having a high boiling point (for example, liquid paraffin, dioctyl phthalate, tricresyl phosphate, silicone oil, etc.) or polymer particles (for example, particles in which at least one of a polymerizable monomer such as styrene, butyl acrylate, divinyl benzene, butyl methacrylate, hydroxyethyl methacrylate, etc. is/are polymerized) each having a solubility in water at room temperature of 0.01% by mass or less. Such oil droplets can be preferably used in an amount in the range of 10 to 50% by mass based on the amount of the hydrophilic binder.

[0033]

In the present invention, to respective layers of the ink-receptive layer, various kinds of conventionally known additives such as a coloring dye, a coloring pigment, a fixing agent of an ink dye, an UV absorber, an antioxidant, a

dispersant of a pigment, an antifoaming agent, a leveling agent, an antiseptic agent, a fluorescent brightener, a viscosity stabilizer, a pH controller, etc. may be further added in addition to the surfactant and the hardener.

[0034]

In the present invention, as the coating method of the respective layers composing the ink-receptive layer is not particularly limited, a coating method conventionally known in the art may be used. For example, there may be mentioned a slide bead system, a curtain system, an extrusion system, an air knife system, a roll coating system, a rod bar coating system, etc.

[0035]

In the present invention, it is preferred to use a system such as a slide bead system wherein the respective layers composing the ink-receptive layer are coated virtually simultaneously without using a drying process whereby required characteristics to the respective layers are obtained with good efficiency, so that it is also preferred in the point of production efficiency. That is, it is expected that, by laminating the respective layers in wet conditions, the components contained in the respective layers are difficultly impregnated into lower layers, so that the component constitution in the respective layers can be well maintained even after drying.

[0036]

A support to be used in the present invention may be mentioned a support in which both surfaces of a base paper are coated with a polyolefin resin such as polyethylene, polypropylene, polyvinyl chloride, a diacetate resin, a triacetate resin, cellophane, an acrylic resin, polyethylene terephthalate, polyethylene naphthalate and the like. By using such a support, higher texture and glossiness are obtained, no wave wrinkle after printing occurs and no head rubbing are caused.

A thickness of the supports is particularly 50 to 300  $\mu\text{m}$

or so, more preferably 180  $\mu\text{m}$  or more to heighten the texture. Also, as a method of rolling a support, it is particularly preferred to use a support rolled with the side to be coated with the ink-receptive layer outside, since the method reduces plus curl of a final ink-jet recording material and causes less head rubbing.

[0037]

When a coating solution for an ink-receptive layer is provided, it is preferred to carry out a corona discharge treatment, flame treatment, UV ray irradiation treatment, plasma treatment and the like prior to provision of the coating.

[0038]

In the present invention, it is preferred to apply a primer layer mainly consisting of natural macromolecules or synthetic resins on a support to be applied an ink-receptive layer.

[0039]

A primer layer to be applied on a support mainly consists of natural macromolecules such as gelatin and casein or synthetic resins. The synthetic resins include acrylic resin, polyester resin, vinylidene chloride, vinyl chloride resin, vinyl acetate resin, polystyrene, polyamide resin, polyurethane resin and the like.

[0040]

The above-mentioned primer layer is applied on a support in a film thickness (dry film thickness) of 0.01 to 5  $\mu\text{m}$ . Preferably, the film thickness is range of 0.05 to 5  $\mu\text{m}$ .

[0041]

In the present invention, it is particularly preferred that an ink-receptive layer is applied on a support and then the ink-receptive layer is rolled with the side of the ink-receptive layer outside, whereby plus curl of final ink-jet recording material is reduced and less head rubbing is caused.

[0042]

To a support in the present invention, various kinds of

back-coat layer can be applied for the purpose of writing property, antistatic property, transportability, prevention of curl or the like. In the back-coat layer, inorganic antistatic agent, organic antistatic agent, hydrophilic binder, latex, pigment, curing agent, surfactant can be contained in optional combination thereof.

[0043]

[Examples]

In the following, the present invention is explained in detail by referring to Examples, but the content of the present invention is not limited by these Examples. Incidentally, "part(s)" and "%" mean "part(s) by mass" and "% by mass" respectively.

[0044]

<Preparation of support A>

A mixture of a bleached kraft pulp of hardwood (LBKP) and a bleached sulfite pulp of softwood (NBSP) with a ratio of 1:1 was subjected to beating until it becomes 300 ml by the Canadian Standard Freeness to prepare a pulp slurry. To the slurry were added alkyl ketene dimer in an amount of 0.5% by mass based on the amount of the pulp as a sizing agent, polyacrylamide in an amount of 1.0% by mass based on the pulp as a strengthening additive of paper, cationic starch in an amount of 2.0% by weight based on the pulp, and a polyamide epichlorohydrin resin in an amount of 0.5% by mass based on the pulp, and the mixture was diluted with water to prepare a 1% slurry. This slurry was subjected to papermaking by a tourdrinier paper machine to have a grammage of 170 g/m<sup>2</sup>, dried and subjected to humidity conditioning to prepare a base paper. A polyethylene resin composition in which 10% by mass of anatase type titanium is dispersed uniformly in a resin of 100% by mass of a low density polyethylene having a density of 0.918 g/cm<sup>3</sup> was melted at 320°C and the melted resin composition was subjected to extrusion coating on the above-mentioned base paper with a thickness of 35 μm by 200 m/min and subjected to extrusion coating by using a cooling roller

which is subjected to slightly roughening treatment. For the other surface of the base paper, a blended resin composition comprising 70 parts by mass of a high density polyethylene resin having a density of 0.962 g/cm<sup>3</sup> and 30 parts by mass of a low density polyethylene resin having a density of 0.918 g/cm<sup>3</sup> was melted similarly at 320°C and the melted resin composition was subjected to extrusion coating with a thickness of 30 μm on the other surface of the base paper and subjected to extrusion coating by using a cooling roller which is subjected to roughening treatment.

[0045]

Subsequently, a surface of the base paper to be applied an ink-receptive layer was subjected to a high frequency corona discharge treatment, and then, a primer layer having the following composition was coated thereon so as to have a gelatin amount of 50 mg/m<sup>2</sup> and dried, which was rolled with the ink-receptive layer side outside to prepare a support A.

[0046]

<Primer layer>

Lime-treated gelatin	100 parts
Sulfosuccinic acid-2-ethyl hexyl ester salt	2 parts
Chromium alum	10 parts

[0047]

A coating liquid for an ink-receptive layer having the composition mentioned below was coated on the above-mentioned support A by a slide bead coating device and dried, and the coated material was rolled with the ink-receptive layer-coated surface outside to prepare an ink-jet recording material A. Incidentally, the fumed silica which is inorganic fine particles was used after dispersing by a high pressure homogenizer with a solid concentration of 20% by mass. Also, the ink-receptive layer was coated so as to have 40 μm thickness of the coating layer after drying. The drying conditions were that the coated material was cooled at 5°C for 30 seconds, dried at 45°C and 10% RH (relative humidity) until a concentration of the total solid concentration became 90% by

mass, and then, at 35°C and 10% RH. A mass ratio of the hydrophilic binder to the inorganic fine particles of this coating liquid was 0.25.

[0048]

<Coating liquid A for ink-receptive layer>

Fumed silica	100 parts
(Average primary particle size: 7 nm)	
Dimethyldiallyl ammonium chloride homopolymer	4 parts
Boric acid	4 parts
Polyvinyl alcohol	25 parts
(Saponification degree: 88%, average polymerization degree: 3500)	
Surfactant	0.3 part

[0049]

The resulting ink-jet recording material A was so cut in a L size (89 mm × 127 mm) that a paper feeding direction of a printer is at right angle to a flowing direction at a time of coating the ink-receptive layer to prepare a ink-jet recording material of Example 1.

[0050]

Example 2

An ink-jet recording material of Example 2 was prepared in the same manner as in Example 1 except for changing a coating liquid for ink-receptive layer of Example 1 to the composition as mentioned below. A mass ratio of the hydrophilic binder to the inorganic fine particles of this coating liquid was 0.20.

[0051]

<Coating liquid B for ink-receptive layer>

Alumina hydrate	100 parts
(Average primary particle size: 15 nm, platy shape with an aspect ratio of 5)	
Boric acid	4 parts
Polyvinyl alcohol	20 parts
(Saponification degree: 88%, average polymerization degree: 3500)	

Surfactant 0.3 part

[0052]

#### Example 3

An ink-jet recording material of Example 3 was prepared in the same manner as in Example 1 except for changing a coating liquid for ink-receptive layer of Example 1 to the composition as mentioned below. A mass ratio of the hydrophilic binder to the inorganic fine particles of this coating liquid was 0.42.

[0053]

<Coating liquid C for ink-receptive layer>

Fumed silica 100 parts

(Average primary particle size: 7 nm)

Dimethyldiallyl ammonium chloride homopolymer 4 parts

Boric acid 4 parts

Polyvinyl alcohol 42 parts

(Saponification degree: 88%, average polymerization degree: 3500)

Surfactant 0.3 part

[0054]

#### Example 4

An ink-jet recording material of Example 4 was prepared in the same manner as in Example 1 except for not using boric acid which is a hardener. A mass ratio of the hydrophilic binder to the inorganic fine particles of this coating liquid was 0.25.

[0055]

#### Example 5

An ink-jet recording material of Example 5 was prepared in the same manner as in Example 1 except rolling the ink-receptive layer with the side on which the ink-receptive layer is coated inside instead of a rolling method for the support and the ink-jet recording material of Example 1. A mass ratio of the hydrophilic binder to the inorganic fine particles of this coating liquid was 0.25.

[0056]

### Comparative Example 1

Onto the base paper of Example 1 was coated a coating liquid for an ink-receptive layer having the composition mentioned below by an air knife coater and dried so as to have a dry mass of 12 g/m<sup>2</sup>. Next, a coating liquid for glossiness developing layer as mentioned below was coated on the ink-receptive layer by an air knife coater so as to have a dry mass of 5 g/m<sup>2</sup>, which was subjected to pressure welding to a mirror surface drum having a surface temperature of 100°C and dried, and peeled off to obtain an ink-jet recording material B. A mass ratio of the hydrophilic binder to the inorganic fine particles of this coating liquid was 0.30.

[0057]

<Coating liquid D for ink-receptive layer>

Wet type synthetic silica	100 parts
(Average primary particle size: 15 nm)	
Polyvinyl alcohol	30 parts
(Saponification degree: 98%, average polymerization degree: 1700)	
Acrylamide cationic polymer	15 parts

[0058]

<Coating liquid for glossiness developing layer>

Colloidal silica	100 parts
(Average primary particle size: 40 nm)	
Polyvinyl alcohol	10 parts
(Saponification degree: 98%, average polymerization degree: 1700)	
Acrylamide cationic polymer	15 parts
Acryl-styrene copolymer	30 parts
Releasing agent	2 parts

[0059]

The resulting ink-jet recording material B was so cut in a Lsize (89 mm × 127 mm) that a paper feeding direction of a printer is at right angle to a flowing direction at a time of coating the ink-receptive layer to prepare a ink-jet recording material of Comparative Example 1.



[0060]

Comparative Example 2

The ink-jet recording material A of Example 1 was so cut in a L size (89 mm × 127 mm) that a paper feeding direction of a printer becomes a flowing direction at a time of coating the ink-receptive layer to prepare a ink-jet recording material of Comparative Example 2.

[0061]

Comparative Example 3

An ink-jet recording material of Comparative Example 3 was prepared in the same manner as in Example 1 except for changing a coating liquid for ink-receptive layer of Example 1 to the composition as mentioned below. A mass ratio of the hydrophilic binder to the inorganic fine particles of this coating liquid was 0.18.

[0062]

<Coating liquid E for ink-receptive layer>

Fumed silica	100 parts
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(Average primary particle size: 50 nm)

Dimethyldiallyl ammonium chloride homopolymer	2 parts
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Boric acid	4 parts
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Polyvinyl alcohol	18 parts
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(Saponification degree: 88%, average polymerization degree: 3500)

Surfactant	0.3 part
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[0063]

For the ink-jet recording materials prepared as mentioned above, evaluation as mentioned below was conducted. The results are shown in Table 1.

[0064]

<Texture and Glossiness>

An image of nature was printed on the respective recording materials by using an ink-jet printer, PM-900C (trade name) manufactured by SEIKO EPSON CO. and compared them with a silver halide photography of the same image of nature. Texture and glossiness were evaluated by feeling with the

following standards.

○: Printed image is comparable to the silver halide photography in the texture and glossiness.

△: Printed image is slightly lower than the silver halide photography in the texture and glossiness.

X: Printed image is clearly inferior to the silver halide photography in the texture and glossiness.

[0065]

<Head rubbing>

The recording materials were humidity conditioned under the circumstance of 13°C, 35% RH for 8 hours. Thereafter, under the same conditions, solid black edgeless printing was carried out each 20 sheets x 5 sets, i.e., total 100 sheets continuously by using an ink-jet printer (manufactured by EPSON CO., PM-780C, trade name), and the situation of head rubbing was observed with naked eyes and evaluated by the following standards.

◎: No head rubbing for all 100 sheets.

○: Slight head rubbing which does not cause any effect on the printed portion was observed in a part of 100 sheets.

△: Head rubbing in which the printed portion became dirt occurred within 10 sheets among 100 sheets.

X: Head rubbing in which the printed portion became dirt occurred more than 10 sheets among 100 sheets, and at worst, scanning of the head stopped.

[0066]

[Table 1]

	Texture and Glossiness	Head rubbing
Example 1	◎	◎
Example 2	◎	◎
Example 3	◎	○
Example 4	◎	○

Example 5	◎	○
Comparative Example 1	△	X
Comparative Example 2	◎	△
Comparative Example 3	△	◎

[0067]

As can be seen from Table 1, it can be understood that Examples 1-5 which are the ink-jet recording materials according to the present invention have better texture and grossiness and give better results regarding the head rubbing than those of Comparative Examples 1-3. Particularly, it can be understood that, in Examples 1 and 2, fumed silica and alumina hydrate were used as inorganic fine particles, a mass ratio of the hydrophilic binder to the inorganic fine particles was 0.40 or less, the hydrophilic binder contains a hardener, and an ink-receptive layer was coated on a support rolled with the side to be coated an ink-receptive layer outside, which was subsequently rolled with the ink-receptive layer outside, whereby better results regarding the ink rubbing were obtained. To the contrary, with respect to Comparative Example 1, grossiness was high due to grossiness developing layer, however, a wave wrinkle occurred after printing and the texture is clearly different from that of a silver halide photograph, and a head rubbing caused frequently due to the wave wrinkle. With respect to Comparative Example 2, the recording material was so cut that a paper feeding direction becomes a flowing direction at a time of coating the ink-receptive layer, whereby head rubbing was likely to occur. With respect to Comparative Example 3, inorganic fine particles having a average primary particle size more than 30 nm were used, whereby grossiness was decreased.

[0068]

[Effects of the invention]

As can be seen from the results mentioned above, in the present invention, an ink-jet recording material having a

particularly good texture and grossiness and causing no head rubbing at the time of printing can be obtained.

[Document name] Abstract

[Summary]

[Problems] An ink-jet recording material having good texture and glossiness and causing no head rubbing at the time of printing can be obtained.

[Solving means] An ink-jet recording material wherein at least one ink-receptive layer is provided on a support in which the both surfaces of a base paper are coated with polyolefin resin, wherein the ink-receptive layer comprises inorganic fine particles having an average primary particle size of 30 nm or less and a hydrophilic binder, and the ink-jet recording material is so cut that a paper feeding direction of a printer is at right angle to a flowing direction at a time of coating the ink-receptive layer.

[Selective figure] None